GORHAM

Volumetric Determination Of Copper

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A NEW VOLUMETRIC DETERMINATION OF COPPER

...BY...

Josiah Gorham

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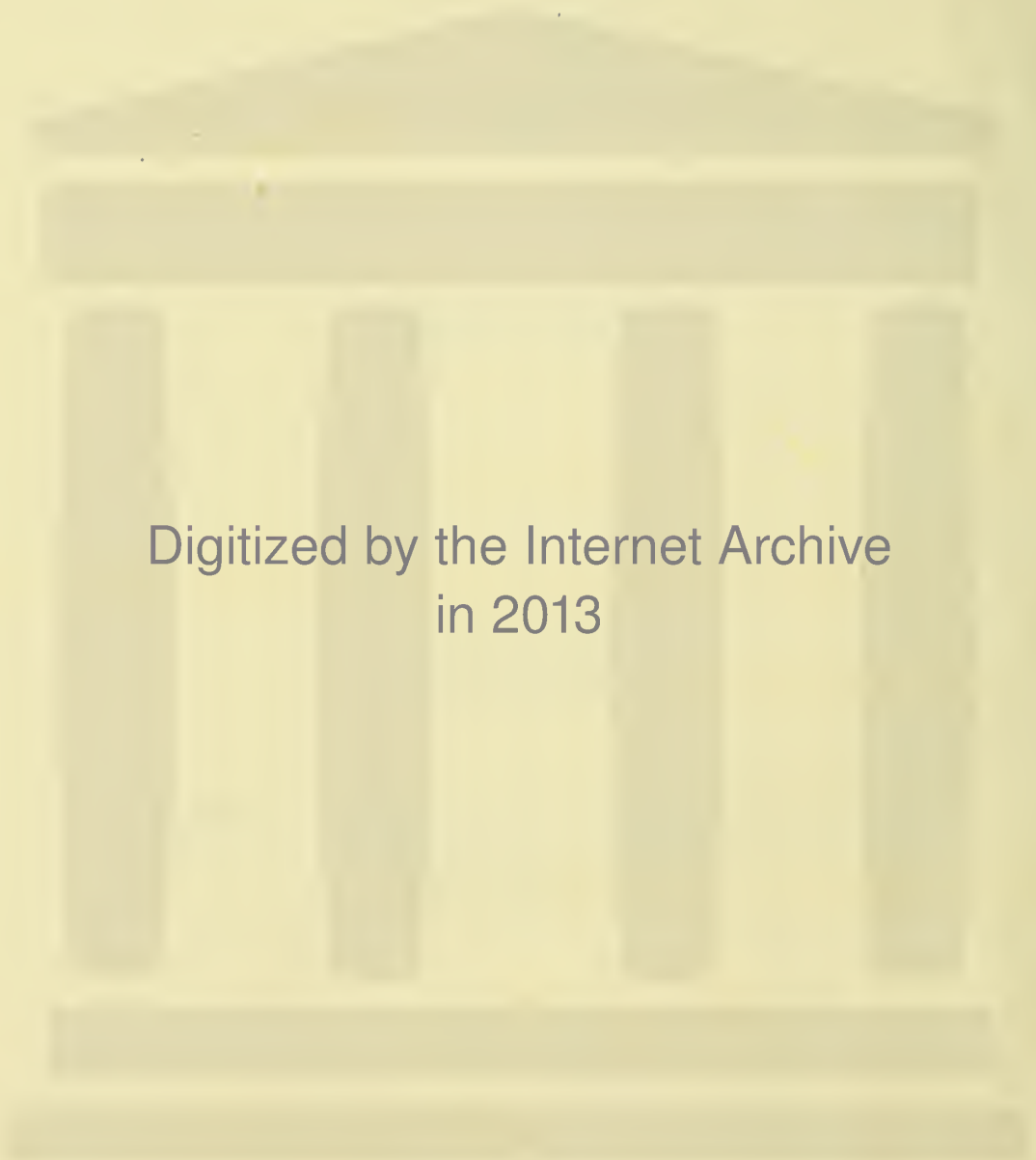

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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OF Bachelor of Science

H. W. Farr

HEAD OF DEPARTMENT OF Applied Chemistry.

A New Volumetric Determination for Copper.

There are at present three well recognized methods employed in the United States for the determination of copper. Each method has its own advocates, and it is perfectly fair to say that either method in the hands of a skilled chemist, thoroughly understanding the reactions of the methods, working with due care will yield substantially the same results. The methods referred to are: 1. The cyanide method. 2. The Iodide. 3. The electrolytic. To these may be added the Parr method and the colorimetric method, the latter being only used for the determination of copper when the percentages fall below two per cent.

The cyanide method depends upon the decoloration of an ammoniacal solution of copper by potassium cyanide. The reaction is such that a double salt of cuprous ammonium cyanide and other compounds are found. The results are influenced by the proportions of copper, of free ammonia and of ammonium salts present, by the bulk of the solution and by the presence of many of the metals other than copper, such as zinc, nickel, manganese, and calcium, also heating the ammoniacal solution while under titration to 40° or 45° C considerably reduces the quantity of cyanide required. R.S.Dublin has suggested that the copper be removed from interfering metals by precipitation as cement copper by aluminium or zinc foil. Owing to the influence exercised by variable quantities of ammonia or its neutral salts upon the decoloration of a copper solution by the cyanide it has been suggested by Beringer to substitute some other alkali for neutralizing the free acid other than ammonia. This suggestion has since been adopted the free acid being neutralized

by sodium carbonate or hydroxide and then on addition of 1 cc.of ammonia-a deep blue solution is at once given which permits of a very sharp end reaction with the cyanide.

The method however is long and there is much liability for error.

The iodide method is most commonly employed in the Lake Superior district and in foreign countries,where it is regarded with much favor. It is based on the fact that when potassium iodide is mixed with a salt of copper in acid solution,cuprous iodide is precipitated as a dirty white powder and iodine set free,thus:

$$2Cu\ SO_4 + KI = Cu_2I_2 + 2I + 2K_2SO_4.$$

The free iodine is then immediately titrated with thiosulphate and starch. A slight modification used in America is described by A. H.Low. He used 20 cc of a saturated solution of zinc acetate to counteract the nitric acid used for dissolving the copper.

As in the cyanide method Dulin's modification is used for separating the copper from interfering metals. The method is not so rapid as the cyanide owing to the time lost at various stages. It is also a little more difficult to manipulate.

The electrolytic method is perhaps the most highly favored in this country. It has the reputation for greatest accuracy. It requires more time than either of the others but since it is easy to regulate the work,so that the battery will precipitate during the night,this is not of so much importance. In regular routine work after solution is effected,the copper should be precipitated with hydrogen sulphide,otherwise many interfering metals are apt to be present and deposited with the copper. The best results are

obtained in a solution containing 20 cc.of strong nitric acid to about 150 cc.solution. Hydrochloric acid and chlorides are not permissible in a solution for quantitative analysis. The presence of organic acids is also inadmissible. The deposit from solutions containing those acids is bright and apparently pure,but the copper is brittle,and contains organic elements.

Before discussing the Parr or Permanganate method it would perhaps be well to look at those methods which make use of the fact that cuprous thiocyanate is precipitated when a neutral or only slightly acid solution of copper nitrate is treated with potassium theocyanate and a reducing agent such as sulphurous acid. The first work done along this line was by Rivot who,after obtaining the insoluble cuprous theocyanate burnt it and weighed the residue as the sulphide. W.F.Carrigues,after obtaining the cuprous thiocyanate ,treated it with an excess of standard alkali. Boiling a few minutes completely changes the cuprous thiocyanate to yellow cuprous hydroxide,thus :

$$2Cu\ CNS + 2\ Na\ O\ H = Cu_2(OH)_2 + 2NaSCN.$$

After filtering off the cuprous hydrate,the filtrate is titrated to neutrality by standard acid and methyl orange.

R.H.Meade treated the cuprous hydrate with an access of ferric chloride or sulphate,together with sulphuric acid. The cuprous hydrate reduces a certain amount of the ferric salt,which is determined by titration with potassium permanganate. The iron equivalent to the permanganate used multiplied by 1.125 gives the weight of copper in the sample.

$$Cu_2(OH)_2 + Fe_2(SO_4)_3 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + 2H_2O.$$

The method although very reliable is too long, requiring three filtrations.

The Parr method invloves the precipitation of copper as the cuprous thiocyanate, the oxidation of the copper without decomposition of the alkali thiocyanate and the titration of the acedified thiocyanate with standard permanganate. The reactions involved are as follows:-

$$2\ Cu.\ O\ H + K\ M\ N O + 2\ Na\ O\ H = 2\ Cu.\ (O\ H)_2 + K_2\ M\ n\ O_4 +$$

$$N\ a_2\ M\ n\ O_4 + 10\ H\ C\ N\ S + 12\ K\ M\ N\ O_4 + 8\ H_2\ S\ O_4 = 10\ H\ C\ N$$

$$+ 6\ K_2\ S\ O + 12 M\ n\ S\ O_4 + 8\ H_2\ O$$

or in one reaction thus:-

$$10\ Cu.\ C\ N\ S + 14\ K\ M\ N\ O_4 + 21\ H_2\ S\ O = 10 Cu.\ S\ O_4 + 7\ K_2$$

$$S\ O_4 + 14\ M\ N\ S\ O_4 + 16\ H_2\ O + 10\ H\ C\ N.$$

Silver is the only metal that is precipitated by the potassium thi cyanate, but it is not affected by the treatment with sodium hydrate and it being insoluble in dilute acids is not readily acted upon by the permanganate. In the precipitation of the Cu C N S an excess of acid must be avoided since the nitric acid tends to prevent the reduction of copper; and excess of such $H_2S\ O_4$ decomposes the thiscyanate and free sulphur is liberated. Thus, after treatment with N a O H is readily acted upon by the permanganate, hence in reducing and precipitating the copper a minimum amount of either acid should be present and better still is sulphuric acid be absent.

The method in detail is as follows:-

A quantity of ore containing about 1/2 gram of copper is digested with 20 c.c. of con. HNO_3. Filter off the insoluble residue and made up the filtrate to 250 c.c. To 10 c.c. of this solution, 2 or 3 c.c. of a 10% K C N S solution and about 5 c.c. of a 10% Na_2SO_3 solution. Heat on water bath until the separation of the white Cu C N S is complete. Filter on asbestos and wash thoroughly. The asbestos pulp and precipitate are returned to the same breaker in which the precipitation was made and treated with 10 c.c. of a 10% K O H. solution. Heat until all the Cu C N S has been converted into Cu O H. Next add the standard permanganate until the green color of the copper is oxidized and none of the C N S radical is acted upon. Warm the mixture and stir until certain that all the copper is oxidized, then add slowly, while stirring, about 30 c.c. dilute H_2SO_4. Heat to 60 degrees or 70 degrees C. and titrate to the usual pink color. Here the C N S radical is acted upon. If an accurate iron factor is known for the permanganate solution, the copper factor may be readily calculated. Each 14 K Mn O_4 molecules are equivalent to 70 Fe or 10 Cu. Therefore we have 10 Cu: 70 Fe: 636: 3920 or 0.1602. Hence the iron factor multiplied by .1602 will give the value in copper.

The first work done was along this line, using a copper solution containing one gram of electrolytic copper (99.6% pure), per liter. Determinations run by this method varied from .2 to .05 c.c. in the titration and in each case somewhat lower than the theoretical titration.

In trying to ascertain what caused this variation the alkali was first considered. For the 10 c. c. of a 10% solution of K O H such alkalis as Na_2CO_3, K_2CO_3, NH_4OH, and Na O H were used. In cases where Na_2CO_3 or K_2CO_3 were used alone the titrations were always several c. c. too low and the end point long in coming, showing that the alkali had not acted thoroughly on the Cu C N S. Where ammonia was used, the titrations were also several c. c. too low. Although the end point came quickly. The low titration here is due to the oxidation of the Cu C N S by the ammonia.

Combinations of these alkalis were next used and the manner and length of heating them varied. Titrations here indicated no improvement and where the mixture was heated a long time (10 - 20 min.) on a water bath or boiled on a plate the titrations were again too low, showing that some oxidation by the air had taken place.

Finding no improvement here the next step was to vary the amount of $KMnO_4$ added to the alkaline solution to oxidize the copper. In cases where more was added than enough to turn the solution green, the titrations were higher. These results are given in the following table:

Table I

c.c. Cu. sol.	c.c KOH 10%	c.c. NaOH 10%	c.c. Na_2CO_3 10%	c.c NH4OH	c.c. KMnO4	Final KMnO4	Theoretical	Remarks.
20	0		10			19.32	19.0	
20	0		10			19.12	19.0	
20	0		10			19.0	19.0	
20	0		10			19.10	19.0	
20	0	10	0		3.0	19.2	19.0	
20		10	0			19.70	19.0	
20			0	0	0	19.0	19.0	
20			0	0	17	22.0	19.0	
20			0	1 cc. 0-11		20.1	19.0	
20	1		0			19.	19.0	
20	10 cc 10% K_2CO_3 sol.					18.3	19.0	
20		10	10		7	21.2	22.3	Boiled on sand bath.
20		10	10		7	22.0	22.3	
20		10	10		8.7	21.0	22.3	
20		10	10		9.7	22.7	22.3	
20		10	10		12.	22.85	22.3	
20		10	10		16	23.7	22.3	
20			10	0	5	22.13	22.3	
20	0		10		3	21.05	22.3	
20	10			KOH_4		18.8	22.3	
20	0			"		19.1	22.3	
20	0					18.15	22.3	
20	0					18.75	19.11	Filtered and titrated filtrate.
20	0					18.7	19.11	"
20	10					18.2	19.11	"
20	10					18.3	19.11	"
20	20					18.0	19.11	"
20	10					18.0	19.11	"
20	10					18.3	19.11	"
20								

From these results it is seen that no improvement can be found on the method as it now stands. The trouble is perhaps due to the oxidation of the copper in the alkaline solution. It was suggested, that if the copper could be oxidized in some way without effecting the C N S radical, it would greatly help. Mr. Johnson has done considerable work in this line, using ammonia and long heating. He found, however, that oxidation by this means was not complete. In a few those determinations run above. I used a small amount of persulphrate after digesting the Cu C N S with alkali. The mixture turned black on standing and the titrations ran low. This suggested that the persulphate had oxidized the cuprous hydrate and had not effected the C N S radical.. In order to test this a solution of K C N S was made up containing about 4 grams of K C N S per liter. The titration with permanganate was obtained and compared with those when the thiocyanate was first treated with a saturated solution of persulphate. It was found here that the titration was not effected when made in the cold, but on warming or heating a considerable decrease in the reading was obtained.

To further test this some titrations were obtained on a determination. The copper thiosulphrate was digested with 10 c, c. 10% K O H on a water bath for 5-10 minutes and then thoroughly cooled. On adding potassium persulphate to this, a black precipitate was found on standing a short time. Acid was now added and the titration obtained. The following are the results:

Table 4

cu. vol	c.c. KOH s. t.	$NaSO_4$	$KMnO_4$	Remarks.
25°	10	2 pcs	11.	
25°	10	2 pcs	17.3	stood one hour before titrating.
25°	5°	crystal	16.2	ammonia was added. end good.
25°	5°	"	16.7	10 c.c. acetone to exclude air.
25°	5°	"	16.4	5 c.c. NH_4OH
25°	5°	"	18.1	" "
25°	5°		18.9	" "
25°	5°	10 cc	18.2	" "
25°	5°	"	18.4	" "
25°	5°		18.2	" " stood ½ hour
25°	5°		17.7	no ammonia. stood ½ hour.

These results, although varying considerable, show that the reaction of the persulphate is constant. Long standings lowers the results on account of the oxidation by the air. Ammonia added in small quantities seems to help the end reaction very much, also hastening the action of the persulphate on the cuprous hydrate. Further determinations were run in this same manner, precipitating and filtering with more care, and varying the conditions.

They are as follows:

Table III

cc. Cu sol.	c. KOH 10%	$K_2S_2O_8$	$KMnO_4$	Remarks.
20°	10	10cc.	18.60	heated on water bath 5
20°	10	5°	5.37	minutes covered. Stood
20°	10	5°	18.2°	to stand for ½ hr
20°	10	10	18.3	minutes after acidifying
20°	10	crystals	18.1	and titrating.
20°	10	"	18.20	"
20°	10	"	18.30	"
20°	10	"	18.18	"
20°	10	"	18.13	"
20°	10		12.72	stirred 5 min.
20°	10		18.	heated on waterbath 40 min.

These last results are more constant and the average is about 18.3. The calculated titration is 19.11 c.c. This difference was at first thought to be due to the action of some hydrogen peroxide formed by the action of the persulphate on the cuprons hydrate. On calculating the amount of peroxide formed by the action of the known amount of copper, it was found to be very large. Enough, in fact, to reduce all the C N S. I am unable to account for this difference. The action of the persulphate may be written thus:-

$$2\ Cu\ O\ H + K_2(S\ O\ )_2 + 2\ K\ O\ H = 2\ Cu\ (O\ H\ )_2 + 2\ K_2\ S\ O_4$$

I next standardized as fresh permanganate solution finding 1 c. c. equal to .00.1208 grams copper. In order to check this up I made determinations on a copper sulphate solution and compared with

the electrolytic results. The following are the results:-

Titration	mg. of copper	electrolytic factor	difference
10.3	18.748	18.521	-.204 mg.
10.3	18.748	18.891	-.140 "
20.30	37.082	37.156	-.077 "
10.75	19.026	18.891	+.135 "
10.75	19.026	18.891	+.135 "
25.90	31.3476	31.4857	-.138 "

The increase in the last two titrations is probably due to some unoxidized cuprous hydrate.

In concluding I would say that determinations run under the same conditions as the standard, give results that compare favorably with any other quick assay for copper.

R E F E R E N C E S .

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